

Linear correlation between surface stress and surface charge in anion adsorption on Au(111)

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Abstract

Voltammetry and quantitative surface stress measurements of anion adsorption on Au(111) have been performed simultaneously at the metal|electrolyte interface. A linear correlation between surface stress and interfacial charge was observed. It is shown that this representation is to be preferred to the usual voltstressogram, since the structure of the latter is dominated by the differential capacity. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Surface stress links the bonding configurations in an interfacial region with its macroscopic properties, for example morphology and thermodynamic behaviour. In surface physics, increasing attention has recently been devoted to reconstruction processes at solid surfaces [1,2] and adsorbate-induced modifications of the bond strength in the topmost substrate layer [3,4]. These microscopic studies of surface stress are obviously also of great interest to electrochemists to whom the unique ability is available to affect the interfacial bonds of single-crystal electrodes by varying the electrode potential. In addition, interest in this topic has been revived by our recent experimental investigations [5–7], which indicate a large difference between the thermodynamic properties of solid and liquid metals in contact with an electrolyte. The controversy [8–14], which has arisen as a result of our findings, will be further addressed in this communication.

2. Experimental

As we have shown recently [5–7], surface stress measurements with an exceptionally high signal-to-noise ratio may be performed in an electrochemical environment by STM. For quantitative studies [3,7,10] the use of a cantilever sample is required, the deflection of which is tracked by the z-piezo. Compared to our previous description [7], the experimental arrangement has been somewhat modified. Due to the surface tension of the electrolyte solution a small circular portion of the liquid may be removed by a syringe in the vicinity of the tip. With this simple procedure the tip remains dry and the electrochemical offset current with its concomitant noise is eliminated. In addition, this enables one to perform measurements under conditions of high current flow. The values of the surface stress changes derived from the Stoney formula [7,15] are corrected for the small area (radius ~ 2 mm) not covered by the solution, with the uncertainty incurred by this procedure being at most 5%. The Au(111) electrodes were evaporated and flame-annealed films (200 nm) on glass cantilever substrates ($9 \times 2 \times 0.55$ mm³) with a thin (2 nm) underlayer of chromium to

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improve adherence [7]. With these dimensions of the sample the surface strain is biaxial (fig. 11 in [15]). The electrode potential was measured with reference to an oxidised gold wire, but the values have been converted to the standard calomel electrode.

We have studied aqueous acid solutions of the perchlorate, sulfate and chloride ions, which exhibit an increasing degree of specific adsorption on metal electrodes. We should like to note that a recent similar investigation [9,10] of perchlorate adsorption on a bulk Au(111) crystal yielded good, although not quantitative agreement with our stress results. Since for evaporated films a certain amount of plastic yield cannot be ruled out we intend to repeat our stress investigations with bulk samples. It is also important to note that our measurements were performed under conditions where the Au(111) surface was kept in the unreconstructed state. Somewhat higher scan rates of the potential were used for this purpose, since the regeneration of the reconstruction is a slow process.

3. Results and discussion

In Fig. 1 a comprehensive set of the various data, which were obtained for all three systems, is presented for the sulfate ion as an example. The small current peaks close to 0.72 V have been shown [16] by STM to be associated with the formation of an ordered sulfate overlayer, with a coverage of 0.2 ML [17]. In Fig. 1b four consecutive scans of the surface stress are superimposed to demonstrate the very low noise of the measurement. With increasing sulfate coverage, as the electrode potential becomes more positive, a compressive surface stress contribution is observed [5–7]. Because of the accuracy of the measurement, the curve can easily be differentiated, to yield the first derivative shown in Fig. 1c.

The similarity between Fig. 1a and c is striking [7] and in sharp contrast to the results obtained with liquid metal electrodes, for which only the second derivative of the surface energy γ is expected to mimic the current [18]. The Lippmann equation, which was derived for a liquid metal, relates γ to the electrode potential E and the charge density σ

$$(\partial\gamma/\partial E)_{T,p,\mu} = -\sigma \quad (1)$$

Provided that the interfacial capacitance C is approximately constant, upon integration of Eq. (1), with $d\sigma = C dE$, a parabolic dependence of the surface energy on either potential or charge is predicted and more or less observed [18].

One purpose of this paper is to show, by direct measurements of the surface stress, that contrary to a previous contention [19], the difference between surface

energy and surface stress of a solid electrode may not be ignored. First, a recent ab-initio calculation [20] for Au(111) and other surfaces predicts that in the Shuttleworth equation [3] γ and its derivative with respect to the surface strain are of comparable magnitude. Indeed for unreconstructed metal surfaces in general, it has been convincingly argued [21] that $(g - \gamma)$ is a significant term. Second, as will be shown below, this is also true for the potential dependence of the difference between these two thermodynamic quantities.

In the following we consider the appropriate electrocapillary equation [19] at constant pressure p , temperature T and chemical potential μ . Due to the high symmetry of the (111)-surface there is no need to retain the tensor notation for the surface stress g and the surface strain ε , and for the sake of brevity we shall subsequently drop the indices p , T and μ for the partial derivatives.

$$d\gamma = -\sigma dE + (g - \gamma) d\varepsilon \quad (2)$$

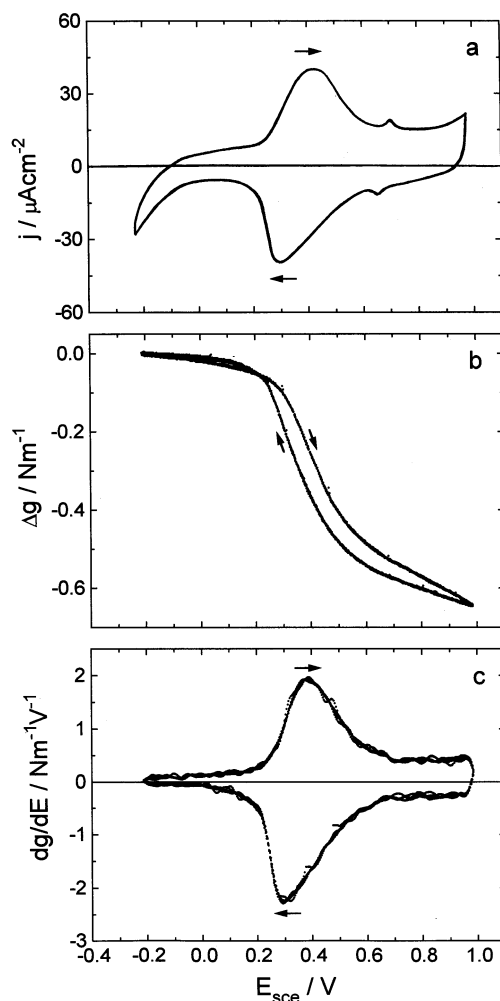


Fig. 1. (a) Voltammogram of Au(111) in 1 M sulfuric acid (scan rate: 200 mV s⁻¹); (b) simultaneous recording of the surface stress change Δg ; (c) first derivative of Δg with respect to electrode potential.

The important point is that under the conditions of constant p , T and μ the surface energy γ , the surface stress g and the charge density σ are functions of the two variables E and ε , only. Since the electrocapillary equation represents a complete differential, one obtains

$$\partial\gamma/\partial\varepsilon = g - \gamma \quad (3)$$

which is the Shuttleworth equation, and

$$\partial\gamma/\partial E = -\sigma \quad (4)$$

which is the Lippmann equation. By differentiating Eq. (3) with respect to E and Eq. (4) with respect to ε we obtain

$$\partial g/\partial E = -\sigma - \partial\sigma/\partial\varepsilon \quad (5)$$

We note in passing that the quantities accessible by experiment are the various functions γ , g , σ and their derivatives along the ‘bending path’ $\varepsilon_b(E)$ of the cantilever in the ε - E plane, for example

$$\gamma^{\text{exp}}(E) = \gamma(E, \varepsilon_b(E)) \quad (6)$$

In principle this implies that one has to consider a line derivative and not just a partial derivative for an exact description of the problem. However, since the various electrostriction terms, which would appear in such a treatment, are all negligible in the standard cantilever configuration [12,14] Eqs. (4) and (5) are sufficiently accurate for an analysis of the data. Nonetheless it is essential to realise that this does not apply to the derivatives with respect to ε in Eqs. (3) and (5).

Another important point for the analysis of our data is that plotting the stress as a function of charge provides a more direct insight into the adsorbate-induced bonding rearrangement at the surface. Since σ is a monotonous function of E the inverse relation is also well defined. Therefore, with $g(E) = g(E(\sigma))$

$$\partial g/\partial E = (\partial g/\partial\sigma)(\partial\sigma/\partial E) \quad (7)$$

Eq. (7) shows that the differential capacity may introduce structure into $\partial g/\partial E$, which is not of primary interest in the present context. A simple model calculation of stress induced by specific adsorption [13] nicely illustrates this dominance of the differential capacity in the potential representation. Similar considerations have been put forward in a theoretical treatment of reconstructions induced by the electrode potential [22].

By on-line integration of the current, it was possible to record g directly as a function of σ (Fig. 2). The pzc has been chosen as 0.25 V for the three ions, as measured for perchlorate [23]. This may not be the real value for the sulfate and chloride ions, but would not change the conclusions put forward here. A potential range has been selected in which the three anions

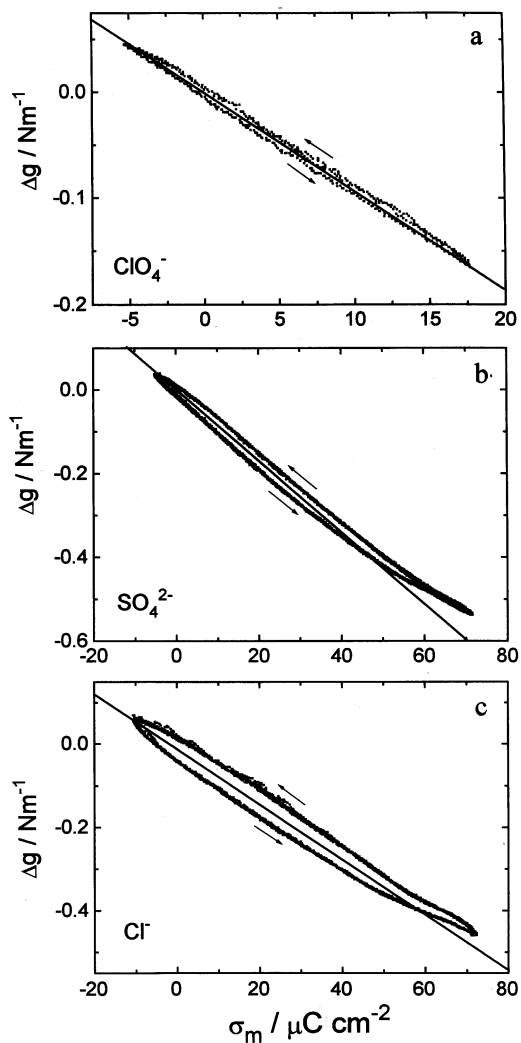


Fig. 2. Dependence of stress change Δg on charge σ : (a) 0.1 M HClO_4 (100–650 mV; 200 mV s^{-1}); (b) 1 M H_2SO_4 (175–950 mV; 200 mV s^{-1}); (c) 0.1 M HClO_4 and 5 mM CsCl (100–825 mV; 500 mV s^{-1}).

increasingly adsorb towards positive potentials. Apart from some excursion into the potential region, where oxide formation commences and which in turn causes some hysteresis (Fig. 2b and c), the surface stress and the charge are found to be linearly correlated. The slopes of these curves are shown in Table 1 and indicate that the values for perchlorate and sulfate are fairly similar, whereas for chloride it is substantially lower.

Curiously, there exists an alternative experimental approach [24] to determine $\partial g/\partial\sigma$ directly, since

Table 1

Values of the slopes $\partial g/\partial\sigma$ for the three anions, obtained from the data in Fig. 2

Anion	ClO_4^-	SO_4^{2-}	Cl^-
Slope/V	-0.91	-0.85	-0.67

$$\begin{aligned} \partial g / \partial \sigma &= (\partial g / \partial E) / (\partial \sigma / \partial E) = -(1 / (\partial \sigma / \partial E)) (\sigma + \partial \sigma / \partial \varepsilon) \\ &= (\partial E / \partial \varepsilon)_Q \end{aligned} \quad (8)$$

(see Appendix A for the derivation of the latter equality). Therefore, it is possible to obtain this quantity by measuring the variation of the open-circuit potential with applied strain [24]. In surface physics language the term $(\partial E / \partial \varepsilon)_Q$ represents the variation of the work function Φ ($\Phi = eE + \text{const}$, where e is the elementary charge) upon deformation of the sample at constant charge. We wish to propose here that a significant factor in determining its behaviour is the change in electron density of the metal substrate due to ε .

In the jellium model [25], this effect may be calculated by making use of the inverse relation between density and strain. Using the data of [25], with $r_s = 3$ (appropriate for gold), we obtain a value of -0.45 V for the slope $d\Phi/d\varepsilon$ at a nearly unstrained surface. Compared to the values in Table 1 this result is of the right sign and order of magnitude, when considering both the crude jellium approximation for gold and the neglect of the double layer. The latter will certainly contribute in an ion-specific manner. Contact can also be made here to surface physics studies, for example the recent first-principles calculation [4] of hydrogen-induced stress on Pt(111). When assigning unit charge to the adsorbate, which is appropriate for discharge from a proton, a slope $\partial g / \partial \sigma$ of -2 V is obtained from the theoretical findings.

4. Conclusions

We have measured surface stress changes due to anion adsorption on Au(111) and found a novel linear correlation with the charge. The dependence of the stress on potential is shown to be masked by any structure in the differential capacity. With reference to surface physics studies we note that, in general, surface energy and surface stress of solid electrodes may not be equated.

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Appendix A

By definition

$$Q(A) = \sigma(E, \varepsilon)A$$

where Q is the total charge on the electrode and A its total area, and

$$\varepsilon = (A - A_0) / A_0$$

where A_0 is some reference value of the electrode area.

Therefore,

$$Q(A) / A_0 = \sigma(E, \varepsilon)(1 + \varepsilon)$$

and

$$dQ / A_0 = (1 + \varepsilon)(\partial \sigma / \partial E)_\varepsilon dE + (\sigma + (1 + \varepsilon)(\partial \sigma / \partial \varepsilon)_E) d\varepsilon$$

We require the total charge to be constant, i.e. $dQ / A_0 = 0$, therefore,

$$(\partial E / \partial \varepsilon)_Q = -(\sigma + \partial \sigma / \partial \varepsilon) / (\partial \sigma / \partial E), \quad \text{for } |\varepsilon_b| \ll 1$$

References

- [1] V. Fiorentini, M. Methfessel, M. Scheffler, Phys. Rev. Lett. 71 (1993) 1051.
- [2] F.K. Men, W.E. Packard, M.B. Webb, Phys. Rev. Lett. 61 (1988) 2469.
- [3] H. Ibach, J. Vac. Sci. Technol. A12 (1994) 2240.
- [4] P.J. Feibelman, Phys. Rev. B 56 (1997) 2175.
- [5] W. Haiss, J.K. Sass, J. Electroanal. Chem. 386 (1995) 267.
- [6] W. Haiss, J.K. Sass, J. Electroanal. Chem. 410 (1996) 119.
- [7] W. Haiss, J.K. Sass, Langmuir 12 (1996) 4311.
- [8] L. Jaeckel, G. Lang, K.E. Heusler, Electrochim. Acta 39 (1994) 1031.
- [9] C.E. Bach, PhD thesis, RWTH Aachen, 1996.
- [10] H. Ibach, C.E. Bach, M. Giesen, A. Grossmann, Surf. Sci. 375 (1997) 107.
- [11] J. Lipkowski, L. Stolberg, in: J. Lipkowski, P.N. Ross (Eds.), Adsorption of Molecules at Metal Electrodes, VCH, Weinheim, 1992, p. 171.
- [12] J. Lipkowski, W. Schmickler, D.M. Kolb, R. Parsons, J. Electroanal. Chem. (in press).
- [13] W. Schmickler, E. Leiva, J. Electroanal. Chem. (in press).
- [14] R. Guidelli, J. Electroanal. Chem. (in press).
- [15] H. Ibach, Surf. Sci. Rep. 29 (1997) 193.
- [16] O.M. Magnussen, J. Haengeboeck, J. Hotlos, R.J. Behm, Faraday Discuss. 94 (1993) 329.
- [17] W. Haiss, PhD thesis, Technical University Berlin, 1994.
- [18] M.A. Habib, J. O'M. Bockris, in: J. O'M. Bockris, B.E. Conway, E.B. Yeager (Eds.), Comprehensive Treatise of Electrochemistry, vol. 1, Plenum, New York, 1980, p. 135.
- [19] D.M. Mohilner, T.R. Beck, J. Phys. Chem. 83 (1979) 1160.
- [20] R.J. Needs, M.J. Godfrey, M. Mansfield, Surf. Sci. 242 (1991) 215.
- [21] D. Wolf, Phys. Rev. Lett. 70 (1993) 627.
- [22] A.A. Kornyshev, I. Vilfan, Phys. Rev. B 47 (1993) 10775.
- [23] B. Roelfs, PhD thesis, Free University Berlin, 1996.
- [24] A.Ya. Gokhshtein, Doklady Phys. Chem. 187 (1969) 492.
- [25] N.D. Lang, in: S. Lundqvist, N.H. March (Eds.), Theory of the Inhomogeneous Electron Gas, Plenum, New York, 1983, p. 309.